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# Catalytic effect of KF-846 on the reforming of the primary intermediates from the co-pyrolysis of pubescens and LDPE

Wen-wu Liu [a,b], Chang-wei Hu [a,*], Dong-mei Tong [a], Yu Yang [a], Gui-ying Li [a], Liang-fang Zhu [a], Jin-Qiang Tang [a]

[a] Key Laboratory of Green Chemistry and Technology, Minister of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu, Sichuan 610064, PR China
[b] Institute of Environmental Science and Engineering, Yibin University, 8 Jiusheng Road, Yibin, Sichuan 644000, PR China

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ABSTRACT

Co-pyrolysis is regarded as an effective approach to upgrade the quality of pyrolysis products. In this work the activity of KF-846 was evaluated by co-pyrolysis of pubescens and low density polyethylene under different experimental conditions including catalytic mode, pyrolytic atmosphere and temperature, etc. The results showed that the fresh KF-846 exerted strong effects of cyclization, aromatization, hydrogen transfer and vapor-catalytic reforming reactions on the primary intermediates from the co-pyrolysis. The hydrogen-rich gases indicated a synergistic effect between Ni and Mo over KF-846 on producing hydrogen. More importantly, the reforming reactions might be inhibited to some extent by $H_2$ atmosphere, the low temperature and the decrease of acidity over catalyst. Furthermore, it was deduced that the oxygen over the lattice of catalyst or some intermediates might transfer into other intermediates, possibly resulting in more products with high oxygen content, but it was presumed that the low temperature, co-pyrolysis process and $N_2$ atmosphere could repress the trend to a certain degree. The mass and energy balance of co-pyrolysis were analyzed, and the main reaction pathways were also proposed. The interference in pyrolysis by regulating the catalytic mode, pyrolytic atmosphere and temperature, acidity over catalyst might posses a certain guiding significance for the pyrolytic technology and the design/selection of catalysts employed.

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## 1. Introduction

Plastics have made a fundamental contribution to our daily activities, but they have caused not only serious environmental problems but also a huge waste of fossil resources, so various recycling methods of waste plastics have been applied in order to solve these problems and produce fuel oil or valuable chemicals. The treatment of waste plastics is commonly divided into two main categories: mechanical recycling such as landfill and chemical recycling including incineration and chemical recycling. [1]. Among the recycling methods the catalytic degradation process is regarded as the most promising method to realize the commercial value of plastics, as the proper catalysts employed can reduce the catalytic temperature and modify the product distribution, providing higher selectivity or improving the yield of products with more commercial interests [2]. At present, the mechanisms of catalytic degradation of waste plastics are mainly focused on a carbonium ion theory, which puts more emphasis on the strength of acid sites over the catalysts applied [3]. In general, it has been reported that the catalysts applied such as zeolites HY, HZSM-5, Hβ and MCM-41. can reduce the activation energy of pyrolytic reactions such as the primary formation of carbocation and the subsequent ones [4–7], the reasons of which are manifold, since the relationship between the catalyst performance and its characteristic, for instance, the strength of acid sites over catalysts, the active species, the pore size distribution, etc. has been suggested by many researchers.

Nowadays biomass is considered as the most common form of renewable energy. Generally, biomass is a complex mixture of hemicellulose, cellulose, and lignin, etc. which is supposed to be pyrolyzed at different rates and by different mechanisms via pyrolysis processes to produce fuels or some useful chemicals [8–10]. However, the bio-oil obtained usually presents some disadvantages such as so high content of water or oxygen that it can not to be used directly as a fuel [11,12]. Therefore, various catalysts and assisting methods have been introduced into the pyrolysis to improve the quality of bio-fuels or chemicals [13–15]. Furthermore, it is deemed that the specific functional catalysts can alter

* Corresponding author. Tel.: +86 28 85411105; fax: +86 28 88835525.
*E-mail address:* Changweihu@scu.edu.cn (C.-w. Hu).

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the products' yield and selectivity. Similarly, more attention is paid in this field to the acidity, active species, and pore architecture over the catalysts employed [16–19].

Many works have been presented concerning the co-pyrolysis of plastics and biomass [20–22]. Co-pyrolysis is esteemed not only a necessity for both environmental protection and sustainable development, but also an effective approach to upgrade the quality of products gained with a less coke formed. Many investigators assume that the waste plastics is characteristic of being cheap, abundantly available and a high hydrogen content, which might provide hydrogen during the co-pyrolysis process and allow for possible chemical interactions between the pyrolytic intermediates, possibly leading to some positive changes in the yield and quality of pyrolysis products. According to the previous works related, most of them focused not only on the primary pyrolysis reactions but also on the secondary vapor-catalytic cracking, occurring homogeneously or heterogeneously outside the reactants [23–25]. It was reported that during the co-pyrolysis some intermediates might react with other intermediates [26], bringing about the formation of phenolic compounds, hydrogen. Moreover, some synergistic effects on producing more valuable products such as bio-oil, hydrogen and phenols were observed [27–29]. Our previous work [28] reported that, in the course of co-pyrolysis of low density polyethylene (LDPE) and pubescens, some intermediates might react with other intermediates with hydroxyl, giving rise to the formation of phenolic compounds, hydrogen and other value-added products, and the synergistic effect on producing hydrogen caused by the combination of Ni and Pd was observed.

It was well-known that during the course of catalytic pyrolysis Ni species over catalysts applied played an important role in the production of hydrogen from biomass [30,31] and/or plastics [32,33]. In addition, our research group had applied some catalysts such as Hβ, H(Na)Y, Pd–$Al_2O_3$, Me-Al-MCM-41 and ZSM-5 in the co-pyrolysis of biomass and plastics, yet the catalyst KF-846 had not been employed, and the correlative research reports were few. Hence, in this work, a commercial catalyst KF-846 with NiO and $MoO_3$ (NiMo/$Al_2O_3$ 3.1 wt.% NiO, 20.7 wt.% $MoO_3$) [34] as its active components, developed by Akzo Co., Netherlands for desulfurization and denitrification in petrochemical engineering at 350–400 °C under high pressure (about 8.0–16.0 MPa), was employed for the catalytic co-pyrolysis of pubescens and LDPE in a fixed bed reactor under normal pressure. The main objective was to examine deeply the catalytic activities of KF-846 related to the production of bio-oil, chemicals and hydrogen as well as the corresponding synergistic effect through varying the experimental conditions like the catalytic modes, cracking temperature or atmosphere.

## 2. Experimental

### 2.1. Raw materials, experimental unit and procedure

The raw materials, experimental units and procedures were similar to those in our previous work [35]. The pubescens was a special kind of biomass and was collected from the Sichuan Province of China (seen in supplementary material 1). Its main components had been determined by our group (mass ratio: cellulose, 28.8%; hemi-cellulose, 19.4%; lignin, 15.3%) [36]. The air-dried pubescens was smashed into powder and then screened to give fraction with the particle size of 360 μm. LDPE employed with a density of 0.9 g/cm$^3$ and an average diameter of 2.2 mm was obtained from Lanzhou Petrochemical Corporation (Lanzhou, China). Prior to the pyrolysis experiments, the pubescens and LDPE samples were subjected to the proximate and ultimate analyses and the results were listed in Table 1. The two raw materials were mechanically mixed before the start of co-pyrolysis. The co-pyrolysis experiments were conducted in a fixed bed reactor with two glass tubes, which bottom of inner tube was sealed for acting as the pyrolytic cell. A fixed catalyst bed made of copper gauze (200 meshes) was designed to investigate the catalytic effect of KF-846 on the secondary reactions. The reactor was heated at a rate of 10 K/min. The co-pyrolysis experiments were performed at 470–450 °C for 2.5 h in $N_2$ or $H_2$ (50 mL/min) with a pubescens-to-LDPE mass ratio of 2 g:8 g i.e. 2:8 under atmospheric pressure. Experiments were made in three replicates to evaluate the standard deviations. Some controlled experiments were also carried out if necessary.

### 2.2. Product analysis

The liquid products and the residue were weighted directly. The yields of liquid, residue and gases plus losses were calculated approximately according to those formulas [35]. The liquid was separated by a separating funnel, the upper phase was defined as "semi oil" (mainly from the pyrolysis of LDPE), and another phase was called "semi aqua" (mainly from pubescens). The yield of semi oil and that of semi aqua were calculated as follows:

$$\text{Yield of semi oil}(\text{wt.\%}) = (\text{weight of semi oil}/\text{weight of LDPE}) \times 100 \tag{1}$$

$$\text{Yield of semi aqua}\,(\text{wt.\%}) = (\text{weight of semi aqua}/\text{weight of pubescens}) \times 100 \tag{2}$$

The composition and relative content (RC) (based on the relative area in the corresponding GC–MS chromatograms) of the products in liquid were analyzed by Agilent 6890 series GC system supplied with a 5973 mass selective detector (USA). The chromatographic conditions applied for the analysis of the pyrolytic products were as follows: stationary phase, 5% of phenyl and 95% of dimethyl polysiloxane; column dimensions, 50 m × 0.25 mm × 0.25 μm. The GC program was: injector temperature, 250 °C; detector temperature, 230 °C; carrier gas, helium; split ratio, 10:1; total flow rate, 16 mL/min. The gases were collected and analyzed by a thermal conductivity detector in temperature programming with separation by gas chromatography (GC) (SP-6800A) by using a column packed with porapak Q (2 m × 3 mm). The peaks corresponding to gases were identified and calculated by comparing retention times with standard gases with known molar percentages of reference compounds, and excluding nitrogen and water from gas composition. With the purpose of the analyses of mass and energy balance of some co-pyrolysis experiments, the ultimate analyses of pyrolysis products including the liquid and residue were carried out to estimate their heat values of combustion (HVC) [22]; especially, the total volume of pyrolysis gas was calculated approximately by dispersion method, that is, the total volume of carrier gas was subtracted from the final total volume of gas; and then the total mole number of the pyrolysis gas was calculated at room temperature and normal pressure using the ideal gas law; finally the mole number of each gas in pyrolysis gas could be calculated on the basis of the results from both their GC analysis and the total mole number.

In order to elucidate the role of each experimental section, a concise flow chart of the research methodologies involved in this work was illustrated in Fig. 1.

### 2.3. Characterization of the catalysts

The acidic properties of the catalysts were examined by $NH_3$-TPD. The sample of 0.1 g was padded in a U-shape steel cell and pretreated in $N_2$ gas at 573 K for 1 h before it was cooled down to 353 K (the adsorption temperature of ammonia). The ammonia

**Table 1**
Proximate and ultimate analysis of the raw materials and the products from non-catalytic co-pyrolysis (NCP) and vapor-catalytic co-pyrolysis (VCP).[a]

| Analysis | Pubescens | LDPE | Semi oil | | Semi aqua | | Residue | | Pyrolysis gas[b] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | NCP | VCP | NCP | VCP | NCP | VCP | NCP | VCP |
| *Proximate analysis* | | | | | | | | | | |
| Moisture (%) | 7.12 ± 0.01 | 0.37 ± 0.001 | /[c] | | / | | / | | / | |
| Volatile matter (%) | 74.98 ± 0.25 | 99.46 ± 0.06 | / | | / | | / | | / | |
| Fixed carbon (%) | 15.45 ± 0.25 | 0.07 ± 0.03 | / | | / | | / | | / | |
| Ash content (%) | 2.49 ± 0.04 | 0.05 ± 0.02 | / | | / | | / | | / | |
| *Ultimate analysis (%)* | | | | | | | | | | |
| C | 47.1 | 84.9 | 79.9 | 81.9 | 47.6 | 43.2 | 90.0 | 91.2 | / | / |
| H | 6.3 | 11.6 | 15.9 | 14.4 | 11.1 | 10.4 | 2.0 | 2.2 | / | / |
| N | 0.4 | 1.7 | / | / | 0.4 | 0.3 | 0.5 | 0.5 | / | / |
| O | 43.7 | / | 0.6 | 0.7 | 38.9 | 45.8 | 4.1 | 3.8 | / | / |
| HVC[d](kJ) | 3363 | 48,800 | 28,239 | 21,286 | 2037 | 1912 | 3413 | 3075 | 12,154 | 7832 |

[a] Reaction conditions: $N_2$, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2:8, ($m_{sample}$:$m_{KF\text{-}846}$ = 10:1 for VCP).
[b] Based on the calculated mole number of each gas in pyrolysis gas.
[c] Not analyzed.
[d] HVC means the heat value of combustion based on the raw materials of 1 kg ($m_{pubescens}$:$m_{LDPE}$ = 2:8).

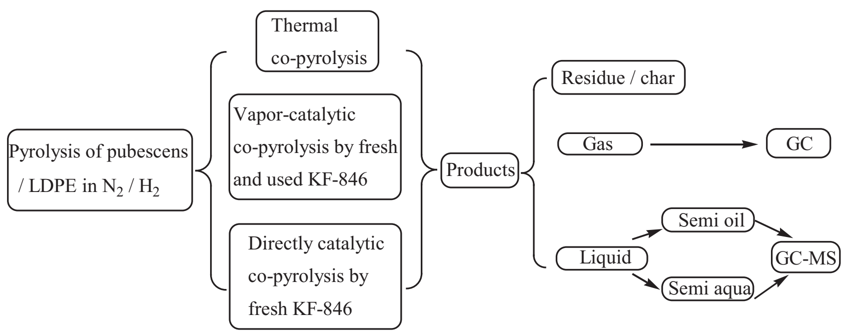



**Fig. 1.** Flow chart of experimental methodology.

gas was introduced into the cell at 353 K for 20 min, and then the physically adsorbed ammonia was removed by purging the samples with He gas for 2.5 h at 373 K. Then the temperature programmed desorption of ammonia was measured with a TCD detector. Ammonia desorption temperatures ranged from 373 to 973 K at a rate of 10 K/min. The X-ray diffraction (XRD) data of KF-846 powder were collected on a Siemens D-5000 diffractometer. Its XRD pattern showed that the KF-846 sample was characteristic of noncrystal, though the characteristic peaks of NiO (a) and $MoO_3$ (b) species were observed narrowly (seen in supplementary material 2).

## 3. Results and discussion

### 3.1. Effect of non-catalytic co-pyrolysis (NCP) and vapor-catalytic co-pyrolysis (VCP) on the yield of products

As shown in Fig. 2, in $N_2$ atmosphere, the yield of liquid, semi oil obtained from the VCP was lower than that from NCP (i.e. the thermal catalytic co-pyrolysis), but that of semi aqua, gas was a little higher than the former's. The reason of which might lie in that the overcracking of semi oil products was promoted significantly by vapor-phase-contact co-pyrolysis. In other words, the improvement in the yields of semi aqua, gas might result from the VCP process at the expense of the yields of liquid and semi oil.

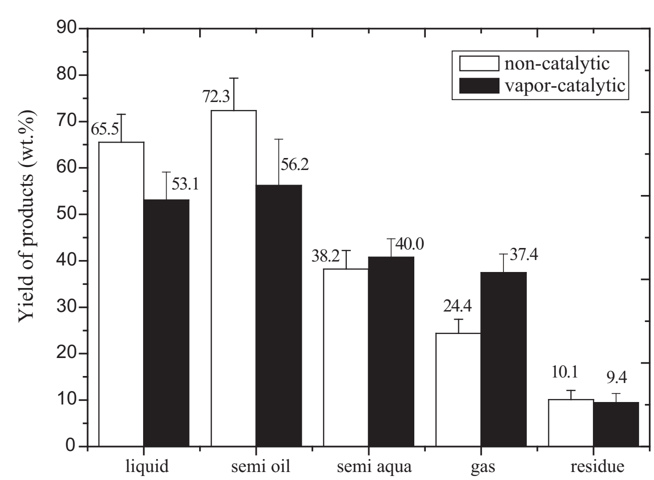



**Fig. 2.** Yield of products obtained under non-catalytic and vapor-catalytic co-pyrolysis conditions ($N_2$, 470–450 °C, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2:8, $m_{sample}$:$m_{KF\text{-}846}$ = 10:1).

### 3.2. Effect of vapor-catalytic reforming in different atmosphere on the relative content (RC) of products

For a clear comparison, the results obtained under the thermal pyrolysis of LDPE in $H_2$ and the NCP of pubescens and LDPE in $N_2$ were also listed in Table 2. For LDPE, it was obviously observed that, even under the vapor-catalytic reforming condition in $H_2$ atmosphere, the pyrolytic intermediates could not be hydrogenated by KF-846, since the RC of unsaturated hydrocarbon in corresponding semi oil was very high. It had been reported that during the catalytic pyrolysis of plastics the reforming catalysts might bring about a higher selectivity to aromatics, probably due to the combination of cracking and reforming activities [37]. The results in Table 2 just testified the conclusion, as the RC of aromatics in semi oil from the thermal pyrolysis of LDPE was only 0.2%, which was much lower than that from the catalytic pyrolysis of LDPE (more than 12%). Moreover, it could be observed that, for the VCP in different

**Table 2**
Effect of catalytic reforming of vapor from co-pyrolysis in different atmosphere on the relative contents of products (%).[a]

| Alkene | Alkane | Cycloparaffin | Aromatics | Acetic acid | Acid∼ester | Aldehyde∼ketone | Furan | Phenol | |
|---|---|---|---|---|---|---|---|---|---|
| $H_2$[b] | 57.7 ± 1.5 | 34.6 ± 1.0 | 7.5 ± 0.6 | 0.2 ± 0.1 | /[d] | / | / | / | / |
| $H_2$ | 31.5 ± 1.5 | 33.8 ± 1.0 | 8.1 ± 0.6 | 26.6 ± 0.1 | 93.2 ± 3.7 | 3.4 ± 0.4 | / | 2.7 ± 0.4 | / |
| $N_2$ | 43.7 ± 1.5 | 33.9 ± 1.0 | 10.1 ± 0.6 | 12.4 ± 0.1 | 85.6 ± 3.7 | 4.3 ± 0.4 | 2.1 ± 0.4 | 3.2 ± 0.4 | 3.9 ± 0.4 |
| $N_2$[c] | 50.4 ± 1.5 | 39.0 ± 1.0 | 7.2 ± 0.6 | 3.5 ± 0.1 | 36.8 ± 3.7 | 10.4 ± 0.4 | 14.7 ± 0.4 | 7.8 ± 0.4 | 26.9 ± 0.4 |

[a] Reaction conditions: 470–450 °C, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2 g:8 g, $m_{sample}$:$m_{KF\text{-}846}$ = 10:1.
[b] Thermal pyrolysis of LDPE only, $m_{LDPE}$ = 8 g.
[c] NCP of pubescens and LDPE, $m_{pubescens}$:$m_{LDPE}$ = 2 g:8 g.
[d] Not detected.

atmosphere, there were some obvious differences in the RC of products in the semi oil between them, especially for alkenes and aromatics. It should be pointed out that, a special phenomenon was observed in the VCP processes, i.e. under the same flow rate of carrier gas (50 mL/min), some of the volatiles from the pyrolytic cell in $N_2$ atmosphere ascended nearly to the upper part of the outer tube, though the status could not be beheld in $H_2$ at all, which might be in relation to the physical properties, particularly the density, of the carrier gas. Accordingly, the residence time of pyrolytic intermediates in $N_2$ atmosphere was a little longer than that in $H_2$ atmosphere. Thereupon, it was presumed that the reactions such as hydrogen transfer in $N_2$, were promoted to a greater extent than that in $H_2$, producing more alkenes and less aromatics. On the other hand, For the pubescens in VCP, the RC of acetic acid (93.2%) obtained in hydrogen was much higher than that (85.6%) in nitrogen, and it was inferred that in $H_2$ atmosphere the reforming reactions of organics such as acetic acid with other molecules were prevented more greatly than that in nitrogen [38], the reasons of which might exist in both the different residence time of intermediates and the strong restraining effect, caused by $H_2$ atmosphere, on the reforming reactions related the formation of hydrogen [28,39,40]. In addition, it was revealed that, especially in the absence of oxygen, the oxygen atoms deoxygenated from some reactants or lattice oxygen over catalysts employed could 'oxidize' other organic molecules [41–45], so according to these views it was speculated that this phenomenon might also lie in the (co-)pyrolysis, that is, the phenomenon probably existed in the vapor-catalyzed (co-)pyrolysis involving pubescens by KF-846 in a non-oxygen atmosphere; moreover, this effect might be outstanding in $H_2$ atmosphere. Additionally, KF-846 was similar to $AgMnO_x$ from the oxide form point of view in a certain degree, as in $AgMnO_x$ sample the oxide AgO species incorporated into $Mn_2O_3$ phase as a mixed Ag–Mn oxide [30]; similarly, the supplementary material 2 demonstrated that there were NiO and $MoO_3$ species in the KF-846 sample. Furthermore, it might be deduced that both the thermal co-pyrolysis and $N_2$ atmosphere could prevent this effect to some extent; sequentially, the reasons might consist in that the chance of oxygen transfer became smaller as a result of the hindrance of intermediates from LDPE during the co-pyrolysis or that the vapor-catalytic reforming reactions were favored by $N_2$ other than $H_2$, which was similar to the results described by Scaccia et al. [38]; namely, during the $N_2$-pyrolysis a larger volume of volatile gases were released from the raw material than that during the $H_2$-pyrolysis. In a word, the main findings related to pyrolytic atmosphere, acidity over catalyst and oxygen transfer might be helpful to the pyrolytic technology as well as the design or selection of catalysts employed.

### 3.3. Influence of temperature on the RC of products in semi oil from VCP

As shown in Fig. 3, with the pyrolytic temperature increasing, the RC of alkene in semi oil increased gradually, while that of alkane decreased rapidly at former stage, then (at about 470 °C) tended to be stable. It was more interesting to observe that the RC of aromatics increased little by little at the beginning of co-pyrolysis, then (at about 470 °C) decreased gradually; and that of cycloparaffin changed similarly with the temperature increasing. The phenomenon revealed the possible mechanism of the catalytic pyrolysis of plastics by fluid catalytic cracking (FCC) catalysts, i.e. a carbonium ion theory [37], which provided a route to cyclization for forming both cycloparaffins and aromatics.

### 3.4. Influence of temperature on the RC of products in semi aqua from VCP

Table 3 showed that, with the temperature increasing, the RC of acetic acid increased from 93.3% to nearly 100% (430–450 °C), then decreased gradually from about 100% to 64.5% (450–490 °C). As for the reason why the RC of acetic acid changed from 93.3% to 64.5%, it might be explained as follows: the effect of oxygen transfer was enhanced gradually by the increase of temperature, but the mechanisms seemed to have changed little by little from 450 °C to 490 °C, as the RC of acetic acid decreased gradually with the increase of temperature, yet that of phenols increased by degrees from 3.0% to 27.6%, the reasons of which might be inferred that although, with the temperature increasing from 450 °C to 490 °C, the effect of oxidation caused by oxygen atoms became strong, the effect of vapor-catalytic reforming reactions became stronger and stronger than the former, which as a whole brought about the results mentioned above. Furthermore, the inference seemed to be confirmed by the corresponding changes of the RC of aromatics, as shown in Fig. 3.

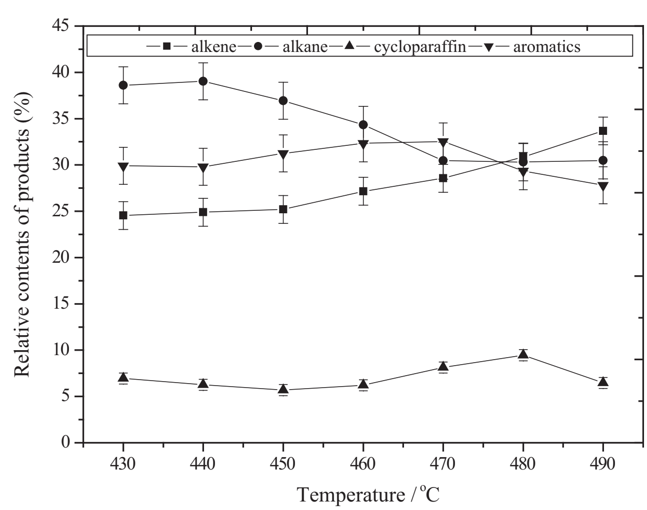



**Fig. 3.** Effect of temperature on the relative content of products in semi oil from the VCP (%) ($N_2$, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2:8, $m_{sample}$:$m_{fresh\ KF\text{-}846}$ = 10:1).

**Table 3**
The influence of temperature on the relative content of products in semi aqua from the VCP (%).[a]

| Temperature (°C) | Acetic acid | Acid~ester | Aldehyde~ketone | Furan | Phenol | Others |
|---|---|---|---|---|---|---|
| 430 | 93.3 ± 3.7 | 3.3 ± 0.4 | 3.4 ± 0.4 | / | / | / |
| 440 | 96.9 ± 3.7 | 3.0 ± 0.4 | / | / | / | / |
| 450 | ~100 ± 3.7 | /[b] | / | / | / | / |
| 460 | 87.2 ± 3.7 | 7.1 ± 0.4 | 2.7 ± 0.4 | / | 3.0 ± 0.4 | / |
| 470 | 79.6 ± 3.7 | 6.3 ± 0.4 | 3.7 ± 0.4 | / | 10.4 ± 0.4 | / |
| 480 | 79.0 ± 3.7 | 3.3 ± 0.4 | 4.2 ± 0.4 | / | 13.5 ± 0.4 | / |
| 490 | 64.5 ± 3.7 | / | / | 7.9 ± 0.4 | 27.6 ± 0.4 | / |

[a] Reaction conditions: $N_2$, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2:8, $m_{sample}$:$m_{KF\text{-}846}$ = 10:1.
[b] Not detected.

It was worth pointing out that the TG–DTG curves of pubescens and LDPE had been determined previously by our group, which indicated that the temperature of pubescens at the end of mass loss was at about 420 °C, while that of LDPE was at about 490 °C (generally speaking, the TG–DTG curves might vary with, to some extent, the conditions of thermogravimetric tests such as the amounts of reactants adopted and the heating rate). Moreover, the co-pyrolysis was conducted in a downdraft reactor. Therefore, the operating temperature in this work was selected at 470–450 °C so as to promote the complete decomposition of reactants as well as energy conservation.

### 3.5. Effect of reuse of catalyst on the yield and RC of products

The catalyst KF-846 used was calcined in air at 500 °C for 4 h to regenerate, that is, to remove the carbon as well as the large molecular weight pyrolysis material (generally called as "coke") depositing/condensing on the catalyst, and then underwent the next repeated run for 5 times. On the whole, the yield of products, the RC of products in semi oil remained almost the same level at different runs. Specifically, the yield of both semi oil and residue increased with the increase of catalyst reused time, yet that of gas decreased. Fig. 4 showed that the RC of aromatics in semi oil increased with the catalyst reusability, yet that of alkane tended to decrease on the contrary; furthermore, all alkane/alkene ratios were more than 1 (between 1.4 and 1.6). What's more, it was interesting to observe that the RC of acetic acid in semi aqua reached nearly 100%, as shown in Table 4, since the catalysts were reused secondly.

The surface acidity of fresh and used KF-846 samples characterized by $NH_3$-TPD was presented in Fig. 5. On the one hand, for fresh KF-846, it seemed that the weak and medium acidic sites were predominant over all the acidic sites, as the amounts of weak and medium acidic sites were 311.6 and 382.1 μmol $NH_3$/g, respectively, while that of strong acidic site was 122.8 μmol $NH_3$/g only. On the other hand, with the increase of reused times, the amount of acid sites gradually decreased, especially for that of strong acidic site, since the amount of strong acidic site over KF-846 fresh and reused for 5 times KF-846 had decreased evidently from 122.8 μmol $NH_3$/g to 55.6 μmol $NH_3$/g. Consequently, it was deduced that the vapor-catalytic reforming reactions related to acetic acid, aromatics, etc. were favored by those strong acidic sites over KF-846; indeed, those specific results observed above such as nearly 100% (RC) of acetic acid in semi aqua, the increasing aromatics in semi oil, etc. could be explained reasonably as follows: with the amounts of strong acid sites decreasing the vapor-catalytic reforming reactions became weaker and weaker, resulting in more semi oil, more aromatics and nearly 100% (RC) of acetic acid as well as more residue, in contrast, less gas. Moreover, it might be presumed that the effects of oxidation by lattice oxygen over KF-846 or some pyrolytic intermediates remained still strong under the VCP by reused KF-846; and the decrease of strong acidic sites over KF-846 had impelled the vapor-catalytic reforming to decrease greatly, which as a whole brought out more aromatics and nearly 100% (RC) of acetic acid.

It was well known that the deposition of coke on the catalyst employed was the main reason leading to the deactivation of catalyst during the pyrolysis [46–48]. The activity of catalyst might decline exponentially with coke content, and the catalyst lost approximately half its activity with a coke content of 4.24% [49]. In a general sense, under the vapor-phase-contact conditions the deposition of coke over catalyst was less serious than that by mixing catalysts directly with pyrolytic materials. In this work, the percentage of coke deposition over KF-846 under VCP conditions was about 24.6 ± 3% (wt.%), which was similar to the results from the catalysis of Fe6/PG and Fe6–Ni3/PG [50] (the molar ratio of Mo to Ni over the fresh KF-846 sample was about 3.5–1). Horne and Williams [47] had found that as the catalysis run time increased the deactivation of the catalyst became apparent, resulting in the decreased yield of monocyclic aromatic hydrocarbons and the increased yield of oxygenated products. It might be said that there were not only some similarities but also some differences between their results and ours in this work. Seeing that the activity of KF-846 decreased obviously with the increasing of catalysis run time, yet the deactivation caused more semi oil, more aromatics and nearly 100% (RC) of acetic acid; consequently, the nearly 100% (RC) of acetic acid might indicate that a strengthened selectivity of products in semi aqua was obtained inadvertently.

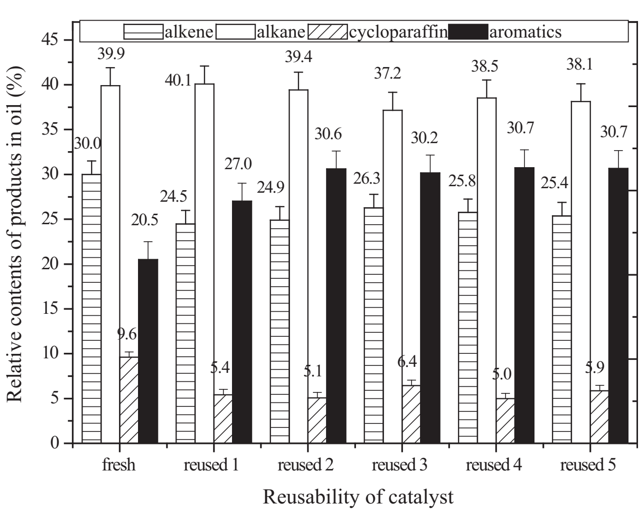



**Fig. 4.** The effect of reuse of catalyst on the relative content of products in semi oil under the VCP condition (%) ($N_2$, 470–450 °C, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2:8, $m_{sample}$:$m_{reused\ KF\text{-}846}$ = 10:1).

### 3.6. Analysis of gaseous products

The gases obtained from VCP, NCP and directly catalyzed co-pyrolysis by KF-846 in $N_2$ were analyzed, and the results were showed in Fig. 6, which illustrated the indirect evidence that the

**Table 4**
The effect of reuse of catalyst on the relative content of products in semi aqua under the vapor catalytic co-pyrolysis condition (%).[a]

| | Acetic acid | Acid∼ester | Aldehyde∼ketone | Furan | Phenol | Others |
|---|---|---|---|---|---|---|
| Fresh | 75.3 ± 3.7 | 5.2 ± 0.4 | / | / | 13.6 ± 0.4 | 5.9 ± 0.4 |
| Reused 1 | 88.6 ± 3.7 | 4.4 ± 0.4 | / | / | 6.3 ± 0.4 | 1.7 ± 0.4 |
| Reused 2 | ∼100 ± 3.7 | /[b] | / | / | / | / |
| Reused 3 | ∼100 ± 3.7 | / | / | / | / | / |
| Reused 4 | ∼100 ± 3.7 | / | / | / | / | / |
| Reused 5 | ∼100 ± 3.7 | / | / | / | / | / |

[a] Reaction conditions: $N_2$, 470–450 °C, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2:8, $m_{sample}$:$m_{KF\text{-}846}$ = 10:1.
[b] Not detected.

hydrogen transfer reactions had happened during the vapor-catalytic cracking. The reasons of which were that, firstly, under the VCP condition the carbonium ions from the pyrolysis of LDPE formed by acidic sites over catalysts easily underwent cyclization reactions, giving rise to the formation of aromatics as well as hydrogen; secondly, some vapor-catalytic reforming reactions had happened in the course of VCP. The most prominent differences shown by Fig. 6 were as follows: A trace of butene was detected in the gaseous mixture from VCP. More importantly, the VCP process had produced the highest volume percentage of hydrogen (about 39.9 vol.%), yet the NCP had contributed the lowest one (about 7.5 vol.%); and the percentage of hydrogen (about 26.4 vol.%) from the directly catalyzed co-pyrolysis was just between them. These facts verified again that those reactions, under the VCP condition, in relation to the cyclization reactions and the vapor-catalytic reforming reactions just mentioned above prevailed among the three co-pyrolysis processes. What is more, compared to the 61.8 vol.% of hydrogen produced by Ni–Pd–Al-MCM-41 [28], it was deduced that there might also be a synergistic effect between Ni and Mo over KF-846 on producing hydrogen, though the effect was not as strong as that created by Ni and Pd over Ni–Pd–Al-MCM-41.

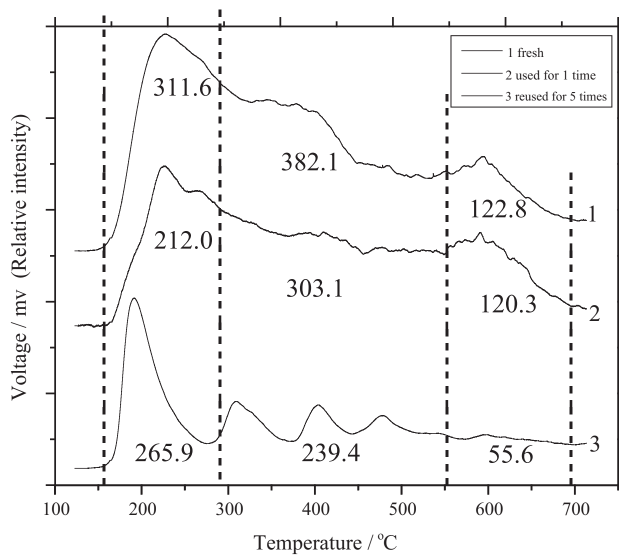



**Fig. 5.** The $NH_3$-TPD profiles of fresh and reused KF-846 (error range: ±20).

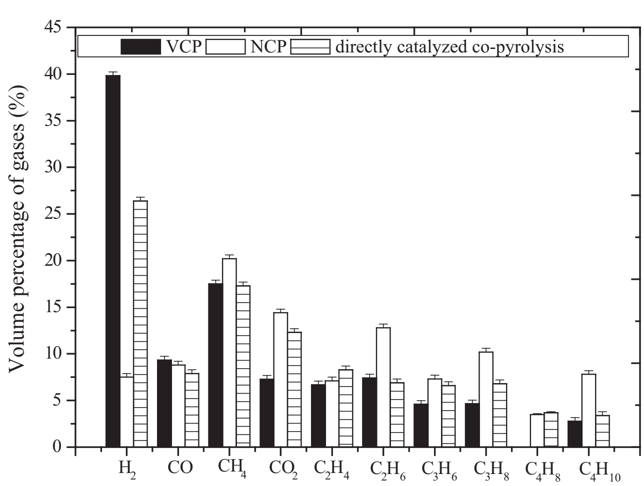


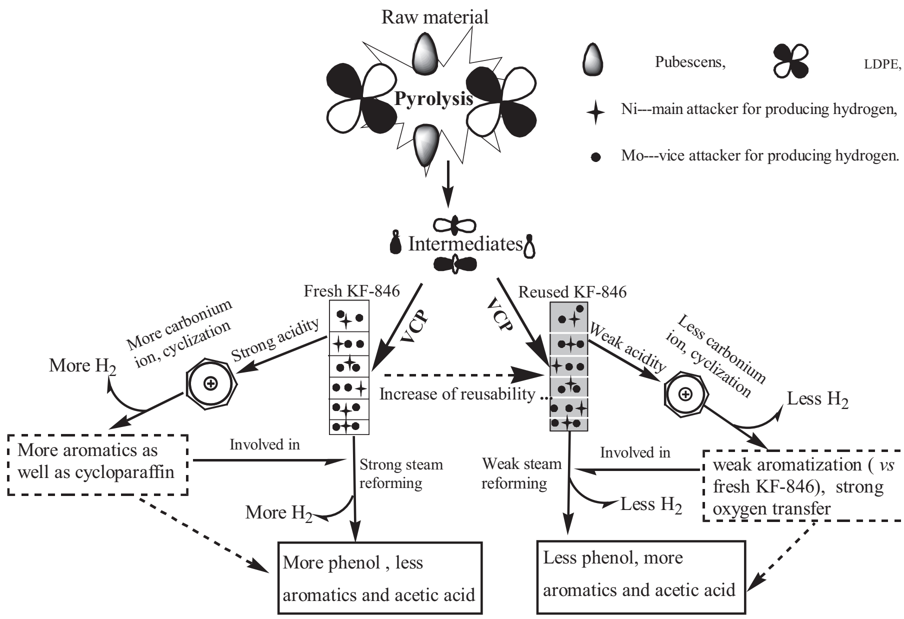

**Fig. 6.** The volume percentage of gases obtained by co-pyrolysis under different conditions. ($N_2$, 470–450 °C, 2.5 h, $m_{pubescens}$:$m_{LDPE}$ = 2:8, $m_{sample}$:$m_{fresh\ KF\text{-}846}$ = 10:1).

### 3.7. Analysis of mass and energy balance for NCP and VCP

As described in Section 2.2, the amounts of residue and liquid produced were determined gravimetrically, and that of pyrolysis gas was calculated approximately. Generally the average mass balance in this work was in the range of 80.5–83.5%. The ultimate analyses of the products including semi oil, semi aqua and residue from NCP and VCP were also listed in Table 1 for the analysis of energy balance. According to the results in Table 1, for the NCP process, the energy balance was about 87.9%; whereas, for the VCP process, it was about 65.4% only. The energy balance in the two processes was relatively low, especially for that of the latter. The reasons of which might be analyzed as follows: for both of them, the energy loss through the walls of the reactor and the lost heat absorbed by the cooling water should be all responsible for the energy unaccounted. And as for 65.4% of the energy balance from the VCP process, it might be rational to attribute its reasons, besides the two points just mentioned, to the strong oxygen transfer from the catalyst sample into the pyrolysis products, resulting in more products with high oxygen content; thus, naturally leading to the lower energy balance.

### 3.8. Scheme of related reactions

The related reaction pathways in this work were proposed in Scheme 1. For fresh KF-846, the effects of carbonium ions, cyclization and vapor-catalytic reforming were prevailing because it embraced stronger acidity than those over used KF-846; moreover, it was worth emphasizing that, for the fresh KF-846 sample, more aromatics as well as acetic acid might participate in the vapor-catalytic reforming reactions, so it produced more phenols, less aromatics and acetic acid finally; furthermore, the effects just mentioned above had promoted the formation of hydrogen to a certain degree. Nevertheless, for reused KF-846, the cases were just the opposite; what is more, it was conjectured that the effect of oxidation by oxygen atoms over used KF-846 or pyrolytic intermediates was obvious under such a situation; reasonably, it was




**Scheme 1.** The reaction pathways proposed.

predicted further that the used KF-846 would produce less hydrogen than the fresh one.

It was well known that the products from the catalytic pyrolysis were mainly influenced by the catalyzing mode, active components, channel structures and strength of acidity, etc. over catalyst employed. In comparison with the results brought out by ZSM-5 zeolite [35], it was found that there were many similarities between them. The reasons for such similarities were analyzed from the following two aspects: for HZSM-5 and fresh KF-846 with a microporous structure as well as a certain amount of strong acidity, both of them favored the aromatization and vapor-catalytic reforming reactions under the VCP condition, resulting in more aromatics or phenols; on the other hand, for DeZSM-5 and reused KF-846, the acidity over them became weak gradually with the increase of desilication or reusability, both resulting in more acetic acid, less phenols as well as more alkane. With regard to the dissimilarity of alkane/alkene ratio (that is, although for both of them all alkane/alkene ratios were more than 1, for all DeZSM-5, the ratios were much higher than 1), the reason of which might be mostly attributed to the different metal species over the two catalysts. For KF-846, it embraced Ni and Mo species so as to favor the formation of hydrogen; but for catalysts ZSM-5, they all produced relatively a little hydrogen, so the alkane/alkene ratio increased greatly with the increase of desilication time. In combination with the results in our previous work [28], it was interesting to draw an analogy that, as described in Scheme 1, during the course of VCP Ni species over the catalyst employed might act as the main attacker for producing hydrogen, while other metals might serve as the vice attacker. In other words, Pd species was an excellent vice attacker, i.e. an excellent promoter in the producing hydrogen from the pyrolysis of biomass/plastics.

## 4. Conclusions

A commercial catalyst KF-846 was employed intensively under the VCP of pubescens and LDPE. According to the results obtained, the following conclusions could be drawn:

(1) The fresh KF-846 exerted strong effects of cyclization, aromatization and hydrogen transfer on the primary intermediates mainly from the pyrolysis of LDPE; the reforming reactions over intermediates were observed affirmatively; the hydrogen-rich gases obtained revealed that there was also a certain synergistic effect on producing hydrogen between Ni and Mo over KF-846.
(2) The lattice oxygen over the catalyst or some intermediates might transfer into other intermediates, resulting in products with high oxygen content, but the specific experimental conditions such as the low temperature, the co-pyrolysis process and $N_2$ atmosphere could repress the trend to a certain degree.
(3) The vapor-catalytic reforming reactions might be inhibited to some extent by the $H_2$ atmosphere, the low temperature and the decrease of acidity over catalyst.

In conclusion, the findings in relation to the interference in the pyrolysis by regulating the catalytic mode, pyrolytic atmosphere and temperature, acidity over catalyst were meaningful, which might be helpful to the pyrolytic technology and the design/selection of catalysts employed.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.enconman.2014.08.028.

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